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TestAmerica, Inc.

US EPA RECORDS CENTER REGION 5
471484

Dayton Division

Standard Operating Procedure

Analyte or Suite: Cyanide, Total

Methodology: Semi-Automated Colorimetric

Reference: Method 335.2 CLP-M, CLP Statement of Work ILM01.0

Revision # 0 Date revised: February 11, 1999

File name: /usr3/sops/WET/Cyanide.VAP

Approvals:

Divisional Manager

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Table of Contents

1. Introduction and Scope

1.1. General.

Preservation: 6 NaOH pellets/L to a pH of 12, refrigerate at 4°C+/-2°C. For soils refrigerate at 4°C+/-2°C

Container: 250cc plastic, glass is also acceptable

Minimum sample volume: 100 mL for Aqueous and 10 grams for Non-aqueous.

Holding Time: 14 days

Range of Test: 0.005 mg/L to 0.500 mg/L for aqueous samples and 0.125 mg/Kg to 12.5 mg/Kg.

Nominal Reporting Limit: 0.005 mg/L (aq); 0.125 mg/Kg (non-aq)

Wavelength Setting: 570 nm

1.2. This SOP can be used to determine the concentration of inorganic cyanide in water, wastewater, saline water, soil, solid, sludge, sediment, and tissue. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. The cyanide in some metal complexes such as cobalt, gold and platinum is not completely recovered. Most organic cyanide compounds, such as nitriles, are decomposed during distillation and are not recovered. This procedure is used to determine values for both total cyanide and cyanide amenable to chlorination.

1.3. "Cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN^-. Cyanide may occur as a free anion (CN^-), as hydrogen cyanide (HCN) or as cyanide compounds. These cyanide compounds are classified as simple and complex cyanides. Simple cyanides form when free cyanide bonds with an alkali, such as sodium or potassium, or a metal, such as iron, copper, or nickel. Complex cyanides contain both alkali and metals.

1.4. Cyanide occurs primarily in industrial effluents. Metal cleaning and electroplating baths, gas scrubbers, gas works, coke ovens, and various other chemical treatments are the main sources of cyanide found in industrial wastes. Theoretically, the cyanide should be destroyed by one of several methods of treatment in the water treatment plant. Natural waters do not contain cyanide, but its common presence indicates that some of it passes through the treatment process into waterways or public systems.

1.5. The generally accepted physiochemical technique for industrial waste treatment of cyanide compounds is alkaline chlorination.

$$NaCN + Cl_2 \rightarrow CNCl + NaCl$$

The first reaction product on chlorination is cyanogen chloride, a highly toxic gas of limited solubility. At an alkaline pH, CNCl hydrolyzes to the cyanate ion, which has only limited toxicity. There is no known natural reduction reaction that may convert cyanate ion to cyanide ion. Breakdown of toxic cyanogen chloride is pH and time dependent. At pH 9, with no excess chlorine present, cyanogen chloride may persist for 24 hours.

1.6. The toxic effects of low concentrations of cyanide on aquatic life and on the biota of wastewater treatment are well established. In lab studies, cyanide concentrations ranging from 0.05-0.15 mg/L have been proven fatal to sensitive species including trout, bluegill, and fathead minnows. Long term exposure to concentrations as low as 0.01 mg/L has been shown to affect the ability of fish to reproduce, grow, and move freely. In humans, high concentrations of cyanide produce rapid respiration leading to breathing difficulties, paralysis, unconsciousness, convulsions, and respiratory arrest. Headache, dizziness, confusion, nausea, and vomiting may occur with lesser concentrations. Chronic exposure over long periods may cause fatigue and weakness. Exposure to 0.50 ppm for 30 minutes may endanger life. Death may result from a few minutes exposure to 300 ppm. The average fatal dose is 50-60 mg.

2. Summary of Method

2.1. The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically by the automated Technicon Traacs 800 Autoanalyzer.

2.2. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, a red-blue color is formed on the addition of pyridine-barbituric acid reagent, which is read through an automated spectrophotometer at 570 nm wavelength. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilutions of the original scrubber solutions to obtain colors of comparable intensity. The automated analysis proceeds as per the manufacturer's industrial method # 802-86T. Sequencing of reagents, flow rates, tray protocols, rate of sample analysis, and all other associated run parameters are as called for by Bran & Luebbe's industrial method # 802-86T, Cyanide In Water And Wastewater.

3. Safety

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. When questions arise, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the TestAmerica Safety Manual. The bottle labels also provide important information that must be noted. If you have any questions, consult your supervisor or safety officer.

Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

The smell of almonds indicates the possible presence of cyanide gas. Take action immediately by clearing the lab area and contacting your safety officer. Samples which smell like almonds should be handled with extreme caution.

4. Reagents and Materials

4.1. Apparatus.

The following apparatus is recommended for performing this procedure. Equivalent items should only be used as a last resort or when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

4.1.1. Bran & Luebbe Technicon Traacs 800 Autoanalyzer with 570 nm filter, 0.5 x 10 mm flowcell.

4.1.2. Miscellaneous autopipetters with appropirate pipet tips.

4.1.3. Miscellaneous Class A glassware including pipets and volumetric flasks.

4.2. Reagents.

The following reagents are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviation from the reagents used in this SOP could be detrimental to the quality of the data produced.

All reagents must be properly labeled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, calibration standards, and dilution water.

4.2.2. Sodium hydroxide 1N: Dissolve 40.00g NaOH in 500 mL deionized water and dilute to 1 liter volumetrically. Shelf life: 1 year

NOTE: This reagent is to be used to acid match calibration standards to prepared samples.

4.2.3. Potassium phosphate monobasic: Dissolve 138g of Potassium phosphate monobasic (KH_2PO_4) in 900 mL of deionized water, and dilute to 1 liter volumetrically. Add 1.0 ml Brij-35 30 % solution. Shelf life: 1 year. This reagent should be refrigerated.

4.2.4. Chloramine-T solution: Dissolve 1.00g of white, water-soluble chloramine-T in 250 mL of deionized water and refrigerate until ready to use. Shelf life: 1 week

4.2.5. Pyridine-barbituric acid reagent: <u>Prepare this reagent in a hood.</u> Place 15g of barbituric acid in a 1000-mL volumetric flask, add just enough deionized water to wash the sides of the flask, and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl, mix, and cool to room temperature. Dilute to 1 liter with deionized water volumetrically and mix. Shelf life: This reagent is stable for approximately six months if stored in a cool, dark place. If precipitate forms, discard reagent and prepare fresh reagent.

4.2.6. Rhodanine indicator: (purchased or) dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone. Shelf life: 1 year

4.2.7. 0.0192N Silver Nitrate: purchased. The use of other normalities of $AgNO_3$ is discouraged. Shelf life: listed by manufacturer. Note: 1 mL = 1 mg

4.2.8. Sodium Arsenite: $NaAsO_2$ crystaline.

<u>4.3. Standards.</u>

The following standards are recommended for performing this procedure. The use of alternative standards will be allowed as long as they are of equal or greater quality and there is an associated improvement in efficiency, productivity, or cost. When instructions are given on how to prepare a specific volume of standard, larger or smaller volumes can be prepared as needed so long as the volumes used are properly documented.

4.3.1. Stock calibrant cyanide standard (1000 mg/L): Premade by manufacturer as Potassium Cyanide.

4.3.1.1. Standardize prior to use and then monthly by using the following procedure. The stock standard solution is titrated with standard silver nitrate ($AgNO_3$) to form the soluble cyanide complex, $Ag(CN)_2^-$. As soon as all CN has been complexed and a small excess of Ag^+ has been added, the excess Ag^+ is detected by the silver-sensitive indicator, p-dimethylaminobenzalrhodanine, which immediately turns from a yellow to a salmon color. The indicator is sensitive to about 0.1 mg Ag/L.

a. Measure 10 mL of 1000 mg/L stock solution into a 150 mL beaker or erlenmeyer flask.

b. Add 15 drops rhodanine indicator to a blank and the sample.

c. Titrate with 0.0192N $AgNO_3$ to first color change from yellow to brownish pink.

d. Calculation:

$$\text{mg/L CN} = \frac{(\text{ml titrant} - \text{mL blank})\left(\frac{1\text{ mg CN}}{1\text{ mL titrant}}\right) \times 1000}{\text{mL of stock standard}}$$

If 0.0192N $AgNO_3$ titrant and 25 mL of standard is titrated, then the calculation reduces to the following:

$$\text{mg/L CN} = (\text{mL titrant} - \text{mL blank}) \times 40$$

If a different normality of titrant is utilized or a different sample volume is used, the long version of the calculation must be performed.

Note: 0.0192N $AgNO_3$ is the proper normality of solution to use as the titrant since 1mL of titrant = 1 mg CN. This is illustrated in the long version of the calculation. Using a titrant of a different normality for performing the standardization procedure is not recommended.

4.3.2. Recommended working calibrant cyanide standard (5.0 mg/L): Prepare by pipetting 5 mL of the Stock 1000 mg/L cyanide standard solution into a 1000 mL volumetric flask and diluting to volume with 0.25N NaOH. Shelf Life 1 Week.

4.3.3. Calibration Standards and Continuing Calibration Verification Standard: Dilute appropriate volumes of the 5.0 mg/L working cyanide standard volumetrically with 0.25N sodium hydroxide (NaOH). The concentration of each standard is calculated from the concentration of the working cyanide standard solution. Shelf life: calibration standards should be prepared fresh daily. A mid-level calibrant is used for the continuing calibration verification. See table below for directions on preparation of the working calibrants.

mls of 5.0 mg/L working stock	concentration in ug/L
#1) 25.0 ml to 250 ml volume	500 ug/L
#2) 15.0 ml to 250 ml volume	300 ug/L
#3) 5.0 ml to 250 ml volume	100 ug/L
#4) 10.0 ml of #2 to 100 ml volume	30 ug/L
#5) 10.0 ml of #3 to 100 ml volume	10 ug/L

4.3.4. Stock alternate source cyanide standard (500 mg/L): Dissolve 0.4907 g of NaCN and 1.00 g NaOH in 400 mL of deionized water and dilute to 500 mL volumetrically.

4.3.5. Working Alternate Source Cyanide Standard (5.00 mg/L): Prepare by pipetting 5 mL of the alternate source 500 mg/L stock into a 500 mL volumetric flask and diluting to volume with 0.25N NaOH. This solution is used as the ICV solution.

4.3.6. Stock cyanide spike solution (5.0 mg/L): Use working source 5.0 mg/L cyanide standard in Section 4.3.2.

4.3.7. Pre-distillation Spiking Procedure: Pipet 1.0 mL of 5.0 mg/L working cyanide spike solution directly through the thistle tube into the 50 mls of sample being distilled. The scrubber solution, which is 0.25N sodium hydroxide, should contain 0.100 mg/L CN if no interferences are observed.

5. Interferences

5.1 Interferences are eliminated or reduced by procedures described in the preparation procedure MIDI.CN.VAP. Interferences observed during the analysis of samples can be eliminated by dilution.

6. Analytical Procedures

6.1. Preservation and Handling.

6.1.1. Samples should be collected in plastic or glass bottles of 250 ml size or larger.

6.1.2. Oxidizing agents, such as chlorine, decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide

(KI)-starch test paper or chlorine test strip; a blue color indicates the need for treatment. Add sodium arsenite a few crystals at a time until a drop of sample produces no color on the indicator.

6.1.3. Samples must be preserved by addition of 6 NaOH pellets per liter of sample, which should raise the sample pH to 12 at the time of collection.

6.1.4. Samples must be refrigerated at 4°C+/-2°C and analyzed immediately if sulfide is present and within 14 days otherwise.

6.2. Instrument Calibration.

6.2.1. Preparation of standard curve per run: The data used in plotting a calibration curve will consist of a blank and five standards evenly distributed throughout the linear range of the method. This data must be collected under the same conditions as those that will exist during routine analyses. Prepare a standard curve by plotting the absorbance values of standards (y-axis) versus the corresponding concentrations (x-axis). Include the blank in the curve.

6.2.2. Calibration criteria - ALL of the following must be met for a successful calibration:

6.2.2.1. A correlation coefficient of 0.995 or greater must be achieved using all calibration standards . The blank is included in the calibration.

6.2.2.2. Verify the curve by analyzing an Initial Calibration Verification Standard (ICVS) and obtaining a value within ± 10% of the true value or within the acceptance ranges established according to averages reported by the independent agency supplying the standard.

6.3. Sample Analysis.

6.3.1. Distillation Procedure For Total Cyanide.

See SOP MIDI.CN.VAP for all appropriate distillation procedures for Total Cyanide.

6.3.2. Automated Spectrophotometric Determination.

6.3.2.1. Refer to the TRAACS Operation manual for instrument preparation.

6.3.2.2. The file name for Cyanide is "cyanide".

6.3.2.3. Tray protocol = P@1,6C>1,H@1,2L@3,1S@7,2I1@8,__S>9,G@1

6.4. Calculation.

6.4.1. Aqueous samples. The instrument print out is in ug/L.

Report the results in mg/L in Labsys.

$$\frac{\text{(results ug/L) X (dilution used)}}{\text{(1000 ug/mg)}} = \text{results mg/L}$$

6.4.2. Solid samples.

$$\frac{\text{(result ug/L) X (250 mL) X (dilution used)}}{\text{(1000 ug/mg) X (weight used)}} = \text{mg/Kg}$$

7. Quality Control.

The following details the QC requirements which apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either instrument performance, method performance (including sample preparation), or individual sample performance. Our goal is to produce data of unquestionable quality. Always remember what purpose the QCI serves when evaluating QCI results. Guidelines can be provided, and are provided, but they cannot take the place of a logical common-sense evaluation of the complete data set.

7.1. Method Detection Limits and Reporting Limits.

An MDL study, following 40 CFR 136, Appendix B, must be done during initial method validation and then annually. If the analytical method is changed, an MDL study must be done again. Also, the calculated MDL must not exceed the reporting limit. The current nominal reporting limit for this parameter is 0.005 mg/L for aqueous and 0.125 mg/Kg for soils.

7.2. Calibration Curve.

7.2.1. Definition and Use of Calibration Curve

The purpose of a calibration curve is to relate instrument response to sample concentration. It also provides a way of verifying that the instrument response, over a predetermined concentration range, can be predicted using a mathematical equation. If the responses were erratic, there would be no accurate way to relate response to concentration. Curves should consist of data containing a blank and five standards. The concentrations of the standards should be distributed over the working range of the curve and they should represent the low, mid, and high points of the curve.

7.2.2. Frequency of Preparing Calibration Curve

When a daily curve system is used, the curve should be re-prepared if during the analytical run a CCV fails and corrective action is unsuccessful.

7.2.3. Criteria for Calibration Curve

Refer to Section 6.2 in this SOP detailing instrument calibration.

7.2.4. Corrective Action for Calibration Curve

Since the calibration curve is used for calculating results for all samples and quality control indicators, an analyte cannot be reported from a run in which the calibration curve did not meet the criteria listed in the SOP. Perform any corrective actions necessary, and re-analyze the curve, the samples, and the quality control indicators.

7.3. Initial Calibration Verification Standard (ICVS).

7.3.1. Definition and Use of ICVS

The purpose of the ICVS is to verify that the standards used to make the curve were chemically pure, prepared properly, and that they have not degraded significantly since the time they were made. The ICVS should be obtained from a different source than the one used to prepare the standards used to construct the curve. The concentration of the ICVS should be at or above the mid point of the range of the analysis. This standard does not go through sample preparation stages. ICVSs can be obtained from a variety of sources including, APG, USEPA, a different lot, or if none of these are available, it may be prepared from the same lot by a different analyst.

7.3.2. Frequency of ICVS

Analyze an ICVS immediately following a calibration curve to verify the curve.

7.3.3. Criteria for ICVS

Acceptance ranges are established according to statistics reported by the independent agency supplying the standard or, if this information is not available, the percent recovery should be within ± 10% of the true value. Caution should be exercised if the statistical range appears to be unusually wide, especially if the analysis is not a trace level analysis. When this is the case, it is recommended that the narrower acceptance criteria of ± 10% be utilized.

7.3.4. Corrective Action for ICVS

If the criteria for the ICVS cannot be met, re-evaluate the calibration curve to verify that all criteria have been met. Verify the acceptability of the source used for preparing the ICVS. Evaluate the concentration of the ICVS compared to the linear range of the analysis and the reporting limit. The concentration of the ICVS should be within the mid to upper range of the curve. If none of the above solves the problem, contact your supervisor before proceeding with the analysis.

7.4. Reagent Blank (RB) / Continuing Calibration Blank (CCB)

7.4.1. Definition and Use of Reagent Blank

The reagent blank is a 0.25N NaOH blank that is subjected to the same conditions that a non-prepared sample undergoes. The reagent blank will determine if any contamination or any memory effects are occurring. Normally, a reagent blank is analyzed every time a CCVS is analyzed.

The reagent blank may contain background color inherent to the analytical procedure, which must be taken into account, during the analytical process.

7.4.2. Frequency of Reagent Blank

Analyze a minimum of one reagent blank at the beginning and one at the end of each analytical batch. Also, analyze a reagent blank after a minimum of every tenth sample.

7.4.3. Criteria for Reagent Blank

Acceptance criteria requires the reagent blank to be less than the reporting limit.

7.4.4. Corrective Action for Reagent Blank

Since the instrument/calculation is zeroed to the reagent blank, a reagent blank after the twentieth sample or at the end of the run having a concentration greater than the reporting limit would indicate a contamination problem or possibly instrument drift. Determine the cause of the high reagent blank value, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair.

7.5. Continuing Calibration Verification Standard (CCVS).

7.5.1. Definition and Use of CCVS

The continuing calibration verification standard is a mid standard that is subjected to the same conditions that a non-prepared sample undergoes. The CCVS will verify that the analytical system is in control with respect to the most recently run calibration curve. Normally, a CCVS is analyzed every time a reagent blank is analyzed.

7.5.2. Frequency of CCVS

Analyze a minimum of one CCVS at the beginning and one at the end of each analytical batch. Also, analyze a CCVS after every tenth sample.

If a five point curve is run daily, the CCVS run at the beginning of the analysis can be part of the curve.

7.5.3. Criteria for CCVS

Acceptance criteria requires the percent recovery to be within 90-110% of the true value, or within the statistically established limits.

7.5.4. Corrective Action for CCVS

Rerun the CCVS, if it is still out of control, determine the cause, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair.

7.6. Preparation Blank (PB).

7.6.1. Definition and Use of PB

The preparation blank is a deionized water blank that is subjected to the same conditions that a prepared sample undergoes. Preparation includes distillation/refluxing. A "clean" preparation blank demonstrates that the preparation procedure is free of contamination.

7.6.2. Frequency of PB

Analyze a minimum of one procedure blank per every twenty distillations.

7.6.3. Criteria for PB

Acceptance criteria requires the procedure blank to be less than the reporting limit. Procedure blanks are not routinely subtracted from the analytical results.

7.6.4. Corrective Action for PB

If a preparation blank shows a detection above the reporting limit for a parameter, then the concentration of the blank vs. the samples in the batch will need to be compared.

If the concentration of the blank is above the reporting limit and a sample is greater than 10x the level of the blank, the sample can be reported with a flag indicating method blank contamination.

If the concentration of the blank is above the reporting limit and a sample concentration is less than 10x the level in the blank, the sample will need to be re-prepared.

If positive values below the reporting limit are observed, they should be evaluated in relation to the sample(s) and extra care should be taken to avoid reporting false positives.

7.7. Lab Control Standard (LCS).

7.7.1. Definition and Use of the LCS

The lab control standard is normally a high or mid standard that is subjected to the same conditions that a prepared sample undergoes. Preparation may include distillation/refluxing. The LCS analysis is designed to serve as a monitor of the efficiency of the entire procedure including sample preparation.

7.7.2. Frequency of LCS

Analyze a minimum of two LCSs of different concentrations per every twenty distillations.

7.7.3. Criteria of LCS

Interim acceptance criteria requires the LCS to be within 85-115% of the true value, or within statistically established limits.

After a data base of 20-30 points has been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s
Upper Warning Limit (UWL) = mean + 2s
Lower Warning Limit (LWL) = mean - 2s
Lower Control Limit (LCL) = mean - 3s

The control limits and warning limits are updated yearly or whenever the process is changed. The data must be plotted on a control chart. If the analysis does not normally require an LCS, then CCVS should be charted instead. The purpose of control charting is to obtain real-time trend analysis of method performance.

7.7.4. Corrective Action for LCS

The inability of the laboratory to successfully analyze the LCS indicates a problem potentially related to the sample preparation procedures. This is especially true if the CCVSs were all in control. If the control windows are exceeded, all sample results associated with the LCS are suspect and should be re-prepared and reanalyzed, after the cause of the problem has been determined and corrected. If reanalysis of the sample occurs outside holding times or if insufficient sample is available for reanalysis, the results must be flagged and the LCS reported to the client.

7.8. Matrix Spike / Matrix Spike Duplicate (MS/MSD).

7.8.1. Definition and Use of MS/MSD

The matrix spike / matrix spike duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The recommended spike concentration should be 20% of the top standard or equal the low or mid standard from a five point curve performed the day of the analysis. These data are generated to determine long-term precision and accuracy of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples except for the sample chosen for the MS/MSD analysis.

7.8.2. Frequency of MS/MSD

Analyze one MS/MSD pair per every twenty distillations per matrix.

7.8.3. Criteria for MS/MSD

7.8.3.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked Sample}) - (\text{Original Sample})}{\text{Spike Value}} \times (100)$$

7.8.3.2. The calculation for Precision as Relative Percent Difference (RPD) is:

$$\text{RPD} = \frac{\text{Difference between Spike Recoveries}}{\text{Mean of the Spike Recoveries}} \times (100)$$

Precision (RPD) must be less than 20%.

Advisory acceptance criteria requires the MS/MSD percent recovery to be within 75-125% and the relative percent difference to be less than 20.

7.8.4. Corrective Action for MS/MSD

No action is taken on out of control MS/MSD data alone to qualify an entire batch. Action taken must be weighed carefully since it may be difficult to determine if poor precision and/or accuracy is a result of sample non-homogeneity/uniqueness, method defects, or laboratory technique. However, the data may be used in conjunction with other QC criteria to determine the need for qualifying the data. If the MS/MSD data is outside acceptance limits, check percent recovery for the LCS. If the LCS is in control, the procedure is in control and the data is acceptable. Potentially, a matrix problem exists. Additional steps may be taken to determine the extent of the matrix interference.

If the concentration of an analyte in the client sample is >4x the level of the spike, then the spiking level is insignificant to the sample and skewed spike recoveries may result. This is not unexpected. Report the results with the appropriate flag.

If an MS/MSD sample is diluted and the concentration of the spiked sample meets the above conditions, then the spike may be diluted out. This also is not unexpected. Report the results with the appropriate flag.

7.9. Daily Analytical Sequence

1. Calibration Curve: five point (per run) curve cc = > 0.995.

2. Initial Calibration Verification Standard (ICVS): 90-110% of the true value. (Must be analyzed for each calibration curve)

3. Reagent Blank (RB): < Reporting Limit or within the statistically established range, at the beginning, at the end, and 1 per every 10 samples.

4. Procedure Blank (PB): < Reporting Limit or within the statistically established range, 1 per every 20 distillations

5. Lab Control Standard (LCS): 80-120% of the true value or within the statistically established range, 2 per batch up to 20 distillations. Samples requiring RCRA analysis must meet 90-100% of the true value for both LCS concentrations.

6. Matrix Spike/Matrix Spike Duplicate: 75-125% and an RPD less than 20 or within the statistically established range, 1 MS/MSD pair every 20 distillations per matrix.

8. Samples 1-10

9. RB

10. CCVS

11. If additional samples are to be analyzed, return to #8...

Always end the sequence with an RB and CCVS

7.10. Data Records and Management

All QC and sample results must be recorded on the cyanide data forms. All maintenance must be documented in the instrument maintenance logs.

8. References

8.1. USEPA Contract Laboraory Program Statement of Work for Inorganics Analysis, Document Number ILM01.0, Part E, Method 335.2 CLP-M

8.2. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020 Revised March 1983.

8.3. Standard Methods For the Examination of Water and Wastewater, 18th Edition, APHA

8.4. Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, November 1990.

8.5. Industrial Method No. 802-86T, Cyanide In Water And Wastewater, Bran & Luebbe Inc., Technicon Traacs 800 Method, August 1986.

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2/11/99

TestAmerica, Inc.

Dayton Division

Standard Operating Procedure

Analyte or Suite: Cyanide, Total

Methodology: Midi Distillation

Reference: EPA 335.2, CLP-M, Statement of Work ILM01.0

Revision # 0 Date revised: February 11, 1999

File name: /usr3/sops/WET/MIDI.CN.VAP

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Table of Contents

1. Introduction and Scope

1.1. General

Preservation: 6 NaOH pellets/L to a pH of 12, refrigerate at 4°C+/-2°C. for aqueous samples. Soils are refrigerated at 4°C+/-2°C.

Container: 250 mL glass or plastic bottle

Minimum sample volume: 100 mL for Aqueous and 10 grams for Non-aqueous.

Holding Time: 14 days

Range of Test: 0.005 mg/L to 0.500 mg/L or 0.125 mg/Kg to 12.5 mg/Kg for non-aqueous samples.

Nominal Reporting Limit: 0.005 mg/L (aq); 0.125 mg/Kg (non-aq)

1.2. This SOP covers the distillation of Cyanide in ground, surface and saline waters, domestic and industrial waste as well as soils.

1.3. "Cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN^-. Cyanide may occur as a free anion (CN^-), as hydrogen cyanide (HCN) or as cyanide compounds. These cyanide compounds are classified as simple and complex cyanides. Simple cyanides form when free cyanide bonds with an alkali, such as sodium or potassium, or a metal, such as iron, copper, or nickel. Complex cyanides contain both alkali and metals.

1.4. Cyanide occurs primarily in industrial effluents. Metal cleaning and electroplating baths, gas scrubbers, gas works, coke ovens, and various other chemical treatments are the main sources of cyanide found in industrial wastes. Theoretically, the cyanide should be destroyed by one of several methods of treatment in the water treatment plant. Natural waters do not contain cyanide, but its common presence indicates that some of it passes through the treatment process into waterways or public systems.

1.5. The generally accepted physiochemical technique for industrial waste treatment of cyanide compounds is alkaline chlorination.

$$NaCN + Cl_2 \rightarrow CNCl + NaCl$$

The first reaction product on chlorination is cyanogen chloride, a highly toxic gas of limited solubility. At an alkaline pH, CNCl hydrolyzes to the cyanate ion, which has only limited toxicity. There is no known natural reduction reaction that may convert cyanate ion to cyanide ion. Breakdown of toxic cyanogen chloride is pH and time dependent. At pH 9, with no excess chlorine present, cyanogen chloride may persist for 24 hours.

1.6. The toxic effects of low concentrations of cyanide on aquatic life and on the biota of wastewater treatment are well established. In lab studies, cyanide concentrations ranging from 0.05-0.15 mg/L have been proven fatal to sensitive species including trout, bluegill, and fathead minnows. Long term exposure to concentrations as low as 0.01 mg/L has been shown to affect the ability of fish to reproduce, grow, and move freely. In humans, high concentrations of cyanide produce rapid respiration leading to breathing difficulties, paralysis, unconsciousness, convulsions, and respiratory arrest. Headache, dizziness, confusion, nausea, and vomiting may occur with lesser concentrations. Chronic exposure over long periods may cause fatigue and weakness. Exposure to 0.50 ppm for 30 minutes may endanger life. Death may result from a few minutes exposure to 300 ppm. The average fatal dose is 50-60 mg.

2. Summary of Method

The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution.

3. Safety

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. When questions arise, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the TestAmerica Safety Manual. The bottle labels also provide important information that must be noted. If you have any questions, consult your supervisor or safety officer.

Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

The smell of almonds indicates the possible presence of cyanide gas. Take action immediately by clearing the lab area and contacting your safety officer. Samples which smell like almonds should be handled with extreme caution.

4. Reagents and Materials

4.1. Apparatus

The following apparatus is recommended for performing this procedure. Equivalent items should only be used as a last resort or when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

4.1.1. Midi Cyanide distillation system including the block digestor and associated glassware.

4.1.2. Diaphragm air compressor or other source of vacuum.

4.1.3. Miscellaneous autopipetters with appropriate pipet tips.

4.1.4. Miscellaneous Class A glassware including pipets and volumetric flasks.

4.2. Reagents

The following reagents are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviation from the reagents used in this SOP could be detrimental to the quality of the data produced.

All reagents must be properly labeled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, calibration standards, and dilution water.

4.2.2. Potassium iodide starch paper.

4.2.3. Bismuth nitrate (0.062 M), $Bi(NO)_3 . 5H_2O$. Dissolve 30 g $Bi(NO)_3.5H_2O$ in 100 mL of water. While stirring add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 L with water.

4.2.4. Sodium hydroxide solution, 10 N: Dissolve 400g of NaOH in deionized water, and dilute to 1 liter volumetrically. Shelf life: 1-3 months.

4.2.5. Sulfamic acid 0.4N: Dissolve 40 g H_2NSO_3H in 1 L of water. Shelf Life: 1 year or expiration date listed by the manufacturer.

4.2.6. Sulfuric acid, 18N: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of deionized water. CAUTION: This is an exothermic reaction. Shelf life: 1 year

4.2.7. Magnesium chloride solution: Weigh 510g of $MgCl_2 \cdot 6H_2O$ into a 1 liter flask, dissolve, and dilute to 1 liter with deionized water volumetrically. Shelf life: 1 year

4.2.8. Sodium Arsenite crystals: $NaAsO_2$

4.2.9. Sodium hydroxide solution, 0.25 N: Dilute 200 mL of 10 N NaOH to 8 liters of DI water. Shelf Life: 3 months.

4.2.10. Lead Acetate Paper

4.3. Standards

The following standards are recommended for performing this procedure. The use of alternative standards will be allowed as long as they are of equal or greater quality and there is an associated improvement in efficiency, productivity, or cost. When instructions are given on how to prepare a specific volume of standard, larger or smaller volumes can be prepared as needed so long as the volumes used are properly documented.

4.3.1. Stock Cyanide standard as Potassium Cyanide (1000 mg/L): Premade by manufacturer.

4.3.2. Working Cyanide Standard (5.00 mg/L): Prepare by pipetting 5 mL of the 1000 mg/L stock into a 1000 mL volumetric flask and diluting to volume with 0.25N NaOH. This solution is used to make digested LCS's, matrix spike/matrix spike duplicates and is the same solution used to prepare calibration curves.

4.3.3. LCS spiking procedure: Add 1 ml of 5 mg/L spike solution to 50 ml DI water and 0.25 N NaOH for a 0.100 mg/L LCS. Add 3 ml of 5 mg/L spiking solution to 50 ml DI water with 0.25 N NaOH for a 0.300 mg/L LCS.

4.3.4. Pre-distillation Spiking Procedure: Pipet 5.0 mL of 5.0 mg/L working source stock cyanide spike solution directly through the thistle tube into the 50 mLs of sample being distilled. The scrubber solution, which is 0.25N sodium hydroxide, should contain 0.100 mg/L CN if no interferences are observed.

5. Interferences

5.1 Oxidized products of sulfide convert CN^- to SCN^- rapidly, especially at high pH. Ideally, treatment for sulfide in an aqueous matrix should occur in the field prior to preserving the sample. If sulfide is a suspected problem, test for S^{-2} by placing a drop of the sample on lead acetate paper that has previously been moistened with acetic acid buffer. Darkening of the paper indicates the presence of S^{-2}. Sulfide interference can be removed by adding Bismuth Nitrate before distillation.

5.2 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid as described in section 6.3.2.9.

5.3. Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

6. Analytical Procedures

6.1. Preservation and Handling

6.1.1. Samples should be collected in plastic or glass bottles of 250 ml size or larger.

6.1.2. Oxidizing agents, such as chlorine, decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI)-starch test paper or chlorine test strip; a blue color indicates the need for treatment. Add sodium arsenite a few crystals at a time until a drop of sample produces no color on the indicator.

6.1.3. Samples must be preserved by addition of 6 NaOH pellets per liter of sample, which should raise the sample pH to 12 at the time of collection.

6.1.4. Samples must be refrigerated at 4°C+/-2°C and analyzed within 14 days.

6.2. Sample Preparation

6.2.1. This distillation procedure can be used on samples that contain up to 10 mg/L CN. If higher levels of CN are expected, a dilution is required before distillation.

6.2.2. Distillation Procedure

NOTE: It is important that the pH for the prep blanks and LCSs be checked to ensure the pH is greater than or equal to 12. If it is not, add more 0.25N NaOH. This is done to ensure the pH matches the pH of the samples.

6.2.2.1. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample by adding 5 mL of 0.062M Bismuth Nitrate to the sample and retest for sulfide. Continue this procedure until sulfide is no longer detected.

6.2.2.2. Place sample into the Midi reflux flask. (50 mL of sample or 50 mL of diluted aliquot or 2.0 grams of solid material diluted to 50 mL with deionized water.

6.2.2.3. Place 50 mL of 0.25N NaOH solution in the Midi absorber flask.

6.2.2.4. Assemble the remaining glass apparatus (Reflux Impinger, Absorber Impinger and the Cold Finger.)

6.2.2.5. Turn on cooling water to condensers (The pressure on the line should be set to 10-15 PSI on the main valve). Make sure that the secondary valve is in the ON position.

6.2.2.6. Turn on the main vacuum.

6.2.2.7. Adjust each vacuum valve to obtain approximately 3 bubbles/second in the reflux flask.

6.2.2.8. Allow the vacuum to draw for about 5 minutes before proceeding with the following steps.

6.2.2.9. Add 5 mL of Sulfamic Acid solution through the air inlet above the reflux flask.

6.2.2.10. Inject 5 mL of Sulfuric Acid through the air inlet above the reflux flask.

6.2.2.11. Inject 2 mL of Magnesium chloride solution through the air inlet. Repeat this step if foaming is noted.

6.2.2.12. Digest the samples in the Midi block for 90 minutes.

6.2.2.13. Turn off the block heater and continue to draw vacuum through the tubes for an additional 15 minutes.

6.2.2.14. When finished allow to cool and turn off vacuum and disconnect the glassware. Transfer the sample in the absorber flask to storage tubes in preparation for Cyanide analysis.

7. Quality Control

The following details the QC requirements which apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either instrument performance, method performance (including sample preparation), or individual sample performance. Our goal is to produce data of unquestionable quality. Always remember what purpose the QCI serves when evaluating QCI results. Guidelines can be provided, and are provided, but they cannot take the place of a logical, common-sense evaluation of the complete data set.

7.1. Method Detection Limits and Reporting Limits

An MDL study, following 40 CFR 136 Appendix B , must be done during initial method validation and then annually. If the analytical method is changed, an MDL study must be done again. Also, the calculated MDL must not exceed the reporting limit. The current nominal reporting limit for this parameter is 0.005 mg/L or 0.125 mg/Kg.

7.2. Preparation Blank (PB).

7.2.1. Definition and Use of PB

The preparation blank is a deionized water blank that is subjected to the same conditions that a prepared sample undergoes. Preparation includes distillation/refluxing. A "clean" preparation blank demonstrates that the preparation procedure is free of contamination.

7.2.2. Frequency of PB

Analyze a minimum of one procedure blank per batch up to twenty distillations.

7.2.3. Criteria for PB

Acceptance criteria requires the procedure blank to be less than the reporting limit. Procedure blanks are not subtracted from the analytical results.

7.2.4. Corrective Action for PB

If a preparation blank shows a detection above the reporting limit for a parameter, then the concentration of the blank vs. the samples in the batch will need to be compared.

If the concentration of the blank is above the reporting limit and a sample is greater than 10x the level of the blank, the sample can be reported with a flag indicating method blank contamination.

If the concentration of the blank is above the reporting limit and a sample concentration is less than 10x the level in the blank, the sample will need to be re-prepared.

If positive values below the reporting limit are observed, they should be evaluated in relation to the sample(s) and extra care should be taken to avoid reporting false positives.

7.3. Lab Control Standard (LCS)

7.3.1. Definition and Use of the LCS

The lab control standard is normally a high or mid standard that is subjected to the same conditions that a prepared sample undergoes. Preparation may include distillation/refluxing. The LCS analysis is designed to serve as a monitor of the efficiency of the entire procedure including sample preparation.

7.3.2. Frequency of LCS

Analyze a minimum of two LCSs of different concentrations per every twenty distillations.

7.3.3. Criteria of LCS

Interim acceptance criteria requires the LCS to be within 85-115% of the true value, or within statistically established limits.

After a data base of 20-30 points has been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s
Upper Warning Limit (UWL) = mean + 2s
Lower Warning Limit (LWL) = mean - 2s
Lower Control Limit (LCL) = mean - 3s

The control limits and warning limits are updated yearly or whenever the process is changed. The data must be plotted on a control chart. The purpose of control charting is to obtain real-time trend analysis of method performance.

7.3.4. Corrective Action for LCS

The inability of the laboratory to successfully analyze the LCS indicates a problem potentially related to the sample preparation procedures. This is especially true if the CCVSs were all in control. If the control windows are exceeded, all sample results associated with the LCS are suspect and should be re-prepared and reanalyzed, after the cause of the problem has been determined and corrected. If reanalysis of the sample occurs outside holding times or if insufficient sample is available for reanalysis, the results must be flagged and the LCS reported to the client.

7.4. Matrix Spike / Matrix Spike Duplicate (MS/MSD)

7.4.1. Definition and Use of MS/MSD

The matrix spike / matrix spike duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The recommended spike concentration should be 20% of the top standard or equal the low or mid standard from a five point curve performed the day of the analysis. These data are generated to determine long-term precision and accuracy of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples except for the sample chosen for the MS/MSD analysis.

7.4.2. Frequency of MS/MSD

Analyze one MS/MSD pair per every twenty distillations per matrix.

7.4.3. Criteria for MS/MSD

7.4.3.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked Sample}) - (\text{Original Sample})}{\text{Spike Value}} \times (100)$$

7.4.3.2. The calculation for Precision as Relative Percent Difference(RPD) is:

$$\text{RPD} = \frac{\text{Difference between two spike recoveries}}{\text{Mean of the spike recoveries}} \times (100)$$

Precision (RPD) must be less than 20%.

Advisory acceptance criteria requires the MS/MSD percent recovery to be within 75-125% and the relative percent difference to be less than 20.

7.4.4. Corrective Action for MS/MSD

No action is taken on out of control MS/MSD data alone to qualify an entire batch. Action taken must be weighed carefully since it may be difficult to determine if poor precision and/or accuracy is a result of sample non-homogeneity/uniqueness, method defects, or laboratory technique. However, the data may be used in conjunction with other QC criteria to determine the need for qualifying the data. If the MS/MSD data is outside acceptance limits, check percent recovery for the LCS. If the LCS is in control, the procedure is in control and the data is acceptable. Potentially, a matrix problem exists. Additional steps may be taken to determine the extent of the matrix interference.

If the concentration of an analyte in the client sample is >4x the level of the spike, then the spiking level is insignificant to the sample and skewed spike recoveries may result. This is not unexpected. Report the results with the appropriate flag.

If an MS/MSD sample is diluted and the concentration of the spiked sample meets the above conditions, then the spike may be diluted out. This also is not unexpected. Report the results with the appropriate flag.

7.5. Data Records and Management

All QC and sample results must be recorded on cyanide data forms. All maintenance performed on the midi-distillation system must be recorded in the instrument maintenance log book.

8. References

8.1. USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis, Document Number ILM01.0, Part E, Method 335.2 CLP-M

8.2. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020 Revised March 1983.

8.3. Standard Methods For the Examination of Water and Wastewater, 18th Edition, APHA

8.4. Industrial Method No. 802-86T, Cyanide In Water And Wastewater, Bran & Luebbe Inc., Technicon Traacs 800 Method, August 1986.

8.5. Instruction Manual, LAB-CREST "MIDI-DIST" Distillation System